

# Electrocatalytic dechlorination of a PCB congener at a palladized granular-graphite-packed electrode: Reaction equilibrium and mechanism

Yuanxiang Fang, Souhail R. Al-Abed\*

National Risk Management Research Laboratory, USEPA, 26 W. Martin Luther King Dr., Cincinnati, OH 45268, United States

Received 6 September 2007; accepted 14 November 2007

Available online 14 January 2008

## Abstract

Our previous study on the electrocatalytic dechlorination of 2-chlorobiphenyl at a Pd-loaded granular graphite-packed electrode demonstrated that the process did not follow the first-order kinetics. The rate constant varied with the applied potential at the beginning, but later became irrelevant to the potential. The electrocatalytic kinetic was investigated in this study, in which several experiments were conducted to dechlorinate 2-chlorobiphenyl using a Pd-loaded granular graphite-packed electrode at different potentials and in methanol–water solutions. Analysis of the experimental results reveals that the electrocatalytic process had reached equilibrium in these experiments. The apparent equilibrium constants, as well as the rate constants for the overall forward and backward reactions, were related to the applied potential. These relationships follow the Tafel equation, but the apparent charge transfer coefficients are very small values. The potential dependence of the overall rate constants suggests a reaction mechanism in which the electrocatalytic reaction is the rate-determining step. The influence of methanol on (together with the potential dependence of) the overall rate constants and the apparent equilibrium constant suggests a Langmuir–Hinshelwood mechanism.

Published by Elsevier B.V.

**Keywords:** Polychlorinated biphenyls (PCBs); Electrocatalytic dechlorination; Kinetics; Equilibrium; Reaction mechanism; Rate law

## 1. Introduction

Polychlorinated biphenyls (PCBs) are toxic persistent organic pollutants in the environment due to their extreme stability and resistance to natural biodegradation. Because of their high hydrophobicity, these compounds tend to accumulate in the biomass along the food chains. Classified as possible carcinogens, they present a potential risk to ecological and human health and such a risk needs to be well managed as soon as possible. Electrocatalytic dechlorination is a promising technology for dechlorinating chlorinated aromatics such as PCBs by removing chlorine atoms from these compounds in non-aqueous solutions [1–4]. The recent development of palladium catalyzed electrochemical dechlorination of chloroaromatics in aqueous media projects a promise of this technology for possible in situ or ex situ remediation of soil,

sediment and groundwater contaminated with chlorinated aromatics [5–10].

Palladium-deposited granular graphite was packed in an electrocatalytic membrane reactor to successfully dechlorinate 2-chlorobiphenyl in an aqueous solution [11]. 2-Chlorobiphenyl (2-CIBP) was selected for the study because its reduction requires a potential higher than almost all the other PCB congeners. The electrocatalytic process was developed to treat PCB laden water-solvent streams that resulted from flushing and washing of PCB-contaminated soils, or to remediate a contaminated plume by deploying the electrode of palladium-loaded granular graphite as a reactive barrier in the field. The rate of 2-CIBP dechlorination observed in the study did not follow the commonly used pseudo-first order kinetics; instead, the apparent rate for the disappearance of 2-chlorobiphenyl decreased significantly over time. According to the temporal profile of the 2-chlorobiphenyl concentration, which always presents two distinct exponential curves, the dechlorination process can be divided approximately into two phases. The rate constant in the first phase varied with the applied

\* Corresponding author. Tel.: +1 513 569 7849; fax: +1 513 569 7879.

E-mail address: [al-abad.souhail@epa.gov](mailto:al-abad.souhail@epa.gov) (S.R. Al-Abed).

potential or the Pd loading, but the rate constant in the second phase had no significant relation with the potential or the Pd loading.

The reason for the shift of reaction rate constant is unknown to the current knowledge of such reactions. For the electrocatalytic dechlorination of 4-chlorophenol in an aqueous medium, Cheng et al. proposed that the dechlorination takes place at the palladium–carbon interface at which the aromatic molecules are adsorbed at the carbon surface and dechlorinated by the active hydrogen species dissolved in the Pd island lattice [5]. This reaction scheme is based on the experimental observations that 4-chlorophenol was dechlorinated at Pd-loaded graphite and carbon felt electrodes but it was not dechlorinated at pure Pd, pure graphite, or pure carbon-cloth electrodes. For the electrocatalytic dechlorination of chloroaromatics in water–methanol medium that contains polyalkylammonium salts, Tsyganok et al. proposed a polyalkylammonium ion ( $R_4N^+$ )-facilitated dechlorination scheme [9]. The chloroaromatic molecules form associates with the  $R_4N^+$  ions in the catholyte, both free and associated ions are adsorbed on the electrode surface, and the molecules that associate with the ions that are adsorbed on the Pd surface or the Pd–substrate interface are dechlorinated by the highly reactive hydrides on the Pd surface. The second reaction scheme does not apply to our previous studies, and the first scheme cannot explain the shift of the rate constant.

The purpose of this work was to investigate the cause for the shift of the apparent rate constant and to obtain in-depth understanding of the electrocatalytic dechlorination process. By using a Pd-loaded granular graphite electrode in a membrane-separated electrochemical reactor, the dechlorination of 2-CIBP was carried out in experiments at different potentials and in solutions that contained different methanol concentrations. While the application of different potentials was expected to cause different dechlorination rates, the use of the solutions with different methanol concentrations was intended to evaluate the influence of the adsorption (and desorption) on the overall dechlorination performance. Based on the experimental data, the electrocatalytic kinetics was studied carefully to determine the cause of the variation of the apparent rate constant, the mechanism and rate expression for the dechlorination of 2-CIBP. The understanding of the dechlorination of 2-CIBP can be indicative of the electrocatalytic processes for the dechlorination of other PCB congeners, as well as other halogenated aromatic compounds, and can help us understand, design, and develop effective treatment processes.

## 2. Material and methods

### 2.1. Chemicals

2-Chlorobiphenyl (purity > 99%), biphenyl (BP) (purity > 99%), standard BP and 2-CIBP solutions in hexane, as well as an internal standard (200 mg L<sup>-1</sup> *d*-8 naphthalene in methylene chloride) were obtained from Ultra Scientific. Palladium acetate ( $CH_3CO_2)_2Pd$  (purity > 98%) was obtained

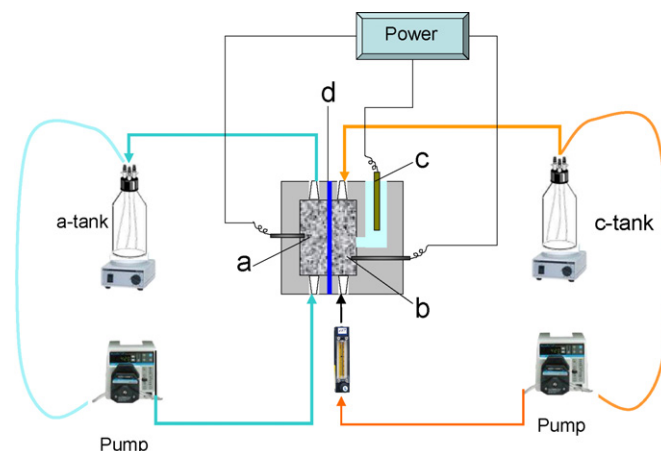


Fig. 1. The membrane-separated electrochemical reactor for PCB dechlorination using granular graphite-packed electrodes: (a) anode; (b) cathode; (c) reference electrode; (d) Nafion<sup>®</sup> membrane [11].

from GFS Chemicals. Granular graphite (30–50 mesh), ammonium acetate (ACS certified), hexane (Optima grade), and acetone (GC grade) were obtained from Fisher Scientific. A cosolvent of acetone and hexane (30:70) was prepared for extraction of organic compounds in water solutions and on granular graphite. Standards of BP and 2-CIBP were prepared from the standard BP and 2-CIBP solutions in hexane. All aqueous solutions were prepared using Milli-Q water (resistivity  $\geq 18 \text{ M}\Omega \text{ cm}$ ).

### 2.2. Electrocatalytic reactor system

The reactor system, shown in Fig. 1, included an electrochemical reactor, a power supply, two solution tanks, and two circulation pumps [11]. The membrane-separated electrochemical reactor consisted of acrylic plastic modules of cathode and anode that were separated by a piece of Nafion<sup>®</sup> membrane. Each module had a void space (in a semi-circular column shape) that could hold about 2.5 g granular graphite. The granular graphite in each module was connected through a 1.5 mm graphite rod to the electric power supply, a potentiostat/galvanostat from Princeton Applied Research (EG&G Instruments, Model 363). To the cathode compartment was attached an  $Ag^+/AgCl$  reference electrode. The cathode and the anode were connected via Teflon tubing to a cathode solution tank (c-tank) and an anode solution tank (a-tank), respectively. The c-tank and a-tank were glass bottles of 250 mL nominal volume and contained electrolyte solutions mixed continuously with magnetic bars; these solutions were circulated by the two peristaltic pumps with special Teflon heads between the c-tank and the cathode and between the anode and the a-tank, respectively. The a-tank was open to the atmosphere. The headspace of the c-tank was connected to a column of Florin to trap any BP and 2-CIBP carried out by the gas generated at the cathode. A port on the cap of the c-tank was available for sampling. Two membrane-separated electrochemical reactors (reactors A and B) were built and used for the experiments in this study.

### 2.3. Electrolytic deposition of palladium

For each experiment, a new piece of Nafion membrane and new granular graphite were used to assemble the membrane reactor. Before Pd deposition, the granular graphite in both cathode and anode was pretreated by soaking the graphite in 1N HNO<sub>3</sub> for 12 h and then by washing the graphite five times with milli-Q water. The electrolytic deposition of Pd was conducted for 7 h at a cathode potential of 0.87 V in 310 mL, 0.1 M NH<sub>4</sub>Ac solution at a circulation flow rate of 15 mL min<sup>-1</sup>. The solution initially contained 0.1347 mM palladium acetate and its pH value was adjusted to 5.0 with acetic acid. The anolyte was a 310 mL 0.1 M NH<sub>4</sub>Ac solution with its pH initially adjusted to 4.2. During the deposition process, samples (1.5 mL) of the cathode solution were taken, diluted to 5 mL with milli-Q water, and analyzed using an IRIS Intrepid ICP spectrometer (thermo-elemental). After completion of the deposition, the cathode was washed with 1 L milli-Q water.

### 2.4. Electrocatalytic dechlorination of 2-chlorobiphenyl

2-CIBP was dechlorinated in the cathode compartment of the electrochemical reactor under different cathode potentials. For each experiment, a new 0.1 M NH<sub>4</sub>Ac PCB-free solution (310 mL) was used in the a-tank, with its pH initially adjusted to a pH value of 4.2. A new 0.1 M NH<sub>4</sub>Ac solution (310 mL), which contained different percentages of methanol, was used in the c-tank. A stock of 2-CIBP in methanol was injected into the c-tank and the solution was mixed for 10 min with the magnetic bar. Dechlorination of 2-CIBP started once a constant cathode potential was applied to the cathode and the catholyte and anolyte were circulated through the cathode and anode, respectively, at a flow rate of 15 mL min<sup>-1</sup>. During the experiment, samples of catholyte (1.5 mL) were taken at specified times, and a duplicate sample was taken randomly at one of these sampling times. At the end, the granular graphite in the cathode was extracted for 18 h with 125 mL cosolvent at room temperature. Following that, the granular graphite was washed with 50 mL methanol.

### 2.5. Analytical methods

The catholyte samples were extracted with 1.5 mL of cosolvent for BP and 2-CIBP for 18 h at 35 °C in a shaker. The samples were centrifuged at a speed of  $5.2 \times g$  (1350 rpm) for 10 min; the extracts, along with the extracts of the cathode graphite, were transferred to 2 mL GC vials. These extracts, after being injected with 10 µL internal standard, were analyzed for BP and 2-CIBP with an HP 5980 GC/MS based on the EPA SW-846 method 8270C for semi volatile organic compounds such as PCBs ([http://www.epa.gov/epaoswer/hazwaste/test/8\\_series.htm](http://www.epa.gov/epaoswer/hazwaste/test/8_series.htm)). The GC/MS was equipped with a Supelco SPB-5 30 m × 0.32 µm × 0.25 µm column; the calibration curves had coefficients of determination ( $r^2$ ) of greater than 0.998 based on 6-point data; the method's detection limit was 50 µg L<sup>-1</sup>. The efficiency of extraction of BP and 2-CIBP from the aqueous solutions was 95%.

## 3. Results

### 3.1. Influence of potential

For the comparison of 2-CIBP dechlorination at different potentials, a cathode of new granular graphite with fresh palladium was used because the dechlorination using the same Pd-loaded granular graphite cathode in a series of consecutive experiments demonstrated a slow decrease in the activity of the electrode. The Pd loading on the granular graphite was about 1.77 mg Pd per g graphite. The palladium in 0.1 M NH<sub>4</sub>Ac was completely deposited on the granular graphite electrode in 7 h (see Section 2.3). The concentration of Pd in the solution decreased exponentially at a rate constant between 0.8 and 1.1 h<sup>-1</sup> and the Pd concentrations at the end of the experiments were below the detection limit (0.1 mg L<sup>-1</sup>). The pH value of the cathode solutions, buffered by NH<sub>4</sub>Ac, increased slightly to less than 8.0 at the end of the experiments. The current decreased significantly in the first half an hour and then decreased gradually throughout the experiments.

Table 1 summarizes the results of 2-CIBP dechlorination using reactors A and B in 0.1 M NH<sub>4</sub>Ac at three cathode potentials. The recovery of biphenyls (BP and 2-CIBP) was calculated by dividing the total amount of BP and 2-CIBP obtained at the end by the initial amount of 2-CIBP. The recovery values varied between 60 and 82% for the experiments using reactor A and between 72 and 92% for the experiments using reactor B. Attempts to enhance recovery by increasing the graphite extraction time to 4 days did not increase recovery values significantly. The extraction of the Florin columns at the end of the experiments did not indicate loss of biphenyls through the gas generated at the cathode. The low recovery values resulted from irreversible adsorption of some of the biphenyls on the granular-graphite, which also was reported in the dechlorination of 4-chlorophenol over carbon-felt electrodes [6].

The three estimates of the 2-CIBP conversion, listed in Table 1, were calculated for each experiment using three different methods. One estimate, calculated based on the amount of BP, is a percentage of biphenyl obtained at the end of the experiment compared to the initial amount of 2-CIBP. The biphenyl-based conversion value is smaller than the actual conversion value because not all biphenyl was recovered at the end of the experiment. Another estimate, based on the removal of 2-CIBP, is the percentage of the 2-CIBP amount eliminated in the experiment. The 2-CIBP-based conversion value is higher than the actual conversion values because the unrecovered portion of 2-CIBP was treated as dechlorinated. A further estimate, based on the distribution of biphenyls, is the percentage of biphenyl among the total amount of biphenyls at the end of the experiment. The distribution-based conversion value is between the biphenyl-based recovery value and the 2-CIBP-based value. Based on all these conversion values (except for the biphenyl-based conversion value for the dechlorination using reactor A at -0.3 V as listed in Table 1), it is obvious that more 2-CIBP was dechlorinated at a higher potential.

Table 1  
Summary of electrocatalytic dechlorination of 2-CIBP: effect of potential and methanol content<sup>a</sup>

$E_C$ (V)	$C_0, C_f$ ( $\mu\text{M}$ )	Recovery (%) <sup>c</sup>	Conversion (%) <sup>d</sup>	$C_{BP}/C_{2-CIBP}$ ( $n$ ) <sup>e</sup>	$k_{adj}$ ( $\text{h}^{-1}$ ) <sup>f</sup>	$K'_R$ <sup>f</sup>	$k'_F$ ( $\text{h}^{-1}$ ) <sup>h</sup>	$k'_B$ ( $\text{h}^{-1}$ ) <sup>h</sup>	$R^2$ (N) <sup>f</sup>
Reactor A									
−0.3	18.9, 2.5	82	37, 46, 56	1.26 (1)	$0.38 \pm 0.01$	1.256 (1.213, 1.268)	$0.213 \pm 0.007$	$0.170 \pm 0.005$	0.999 (9)
−0.5	19.5, 1.0	60	36, 60, 76	$2.5 \pm 0.1$ (6)	$0.46 \pm 0.02$	2.705 (2.624, 2.854)	$0.334 \pm 0.011$	$0.124 \pm 0.004$	0.998 (10)
−0.87	12.9, 0.2	78	70, 90, 92	$27.6 \pm 1.2$ (3)	$0.87 \pm 0.08$	28.56 (28.34, 32.08)	$0.839 \pm 0.079$	$0.029 \pm 0.003$	0.988 (8)
Methanol (%) <sup>b</sup>									
10	16.9, 0.8	77	59, 77, 82	$5.491 \pm 0.294$ (4)	$0.353 \pm 0.008$	5.918 (5.835, 6.214)	$0.302 \pm 0.007$	$0.051 \pm 0.001$	0.999 (10)
20	17.8, 4.6	74	23, 31, 49	$0.500 \pm 0.026$ (5)	$0.388 \pm 0.024$	0.525 (0.506, 0.562)	$0.134 \pm 0.008$	$0.254 \pm 0.016$	0.995 (8)
30	17.8, 7.8	83	22, 26, 39	$0.335 \pm 0.010$ (6)	$0.437 \pm 0.021$	0.336 (0.333, 0.341)	$0.102 \pm 0.05$	$0.298 \pm 0.016$	0.996 (9)
Reactor B									
−0.3	11.2, 1.4	75	27, 36, 52	$0.73 \pm 0.04$ (4)	$0.39 \pm 0.02$	0.755 (0.751, 0.763)	$0.150 \pm 0.010$	$0.192 \pm 0.013$	0.999 (9)
−0.5	17.9, 0.4	72	58, 81, 86	$4.04 \pm 0.09$ (4)	$0.46 \pm 0.03$	4.100 (4.030, 4.301)	$0.373 \pm 0.025$	$0.091 \pm 0.006$	0.993 (9)
−0.65	15.6, 0.1	92	83, 90, 91	$37.78 \pm 0.96$ (4)	$0.80 \pm 0.03$	38.69 (38.61, 38.70)	$0.784 \pm 0.025$	$0.020 \pm 0.001$	0.999 (7)

g-Values and their 95% confidence intervals of the overall rate constants for forward ( $k'_F$ ) and backward ( $k'_B$ ) reactions.

<sup>a</sup> Conditions for all the experiments of dechlorination using reactors A and B: 2.5 g granular-graphite packed cathode deposited with 1.77 mg Pd/g graphite; 310 mL 0.1 M  $\text{NH}_4\text{Ac}$  solution; circulation flow rate =  $15 \text{ mL min}^{-1}$ ;  $23^\circ\text{C}$ ; 101 kPa.  $E_C$  (V) is the applied cathode potentials.  $C_0$  and  $C_f$  ( $\mu\text{M}$ ) is the initial and final concentrations of 2-CIBP in the solution, respectively.

<sup>b</sup> Experiments were conducted at  $E_C = -0.5 \text{ V}$  in 0.1 M  $\text{NH}_4\text{Ac}$  solutions with different percentages of methanol.

<sup>c</sup> The value of recovery is the percentage of the total amount of (dissolved and adsorbed) biphenyls obtained at the end compared to the initial amount of 2-CIBP.

<sup>d</sup> Three estimates for 2-CIBP conversion: The first is the percentage of the amount of BP measured at the end compared to the initial amount of 2-CIBP; the second is the percentage of BP in the amount of biphenyls measured at the end; and the third is the percentage of 2-CIBP removed in the experiment

<sup>e</sup> The average and standard deviation of the BP to 2-CIBP concentration ratio in the last  $n$  samples.

<sup>f</sup> The adjusted rate constant  $k_{adj}$  and apparent reaction equilibrium constant  $K'_R$  were obtained by best fitting the  $N$  points of the  $C_{2-CIBP} - C_{BP}/K'_R$  data to an exponential line with a maximum  $R^2$  value. Two values of  $K'_R$  in the bracket is the range of  $K'_R$  values that resulted in the residue sum of squares (ssresid) less than 150% of the ssresid with the  $K'_R$  value.

The rate of decrease in 2-CIBP concentration during the experiments varied and the change of 2-CIBP concentration presented two stages that had distinctively different rate constant values, which is similar to our previous results [11]. The rate constant values in the first stage increased with an increase in the applied cathode potential, but there was no clear trend in the values of the rate constant in the second stage. These characteristics are demonstrated clearly in Fig. 2(a) and (b), which present the concentrations of 2-CIBP and BP in 0.1 M  $\text{NH}_4\text{Ac}$  in the experiment of dechlorination at  $-0.5 \text{ V}$ .

An interesting feature, characteristic of all the results of dechlorination at different potentials, is that the ratio of the biphenyl to 2-CIBP concentrations reached a fairly constant value in the second stage. Table 1 lists the average and standard deviation values of the concentration ratio for the last few samples in these dechlorination experiments. These ratio values increased with an increasing potential.

### 3.2. Influence of methanol

The influence of methanol on the electrocatalytic dechlorination was evaluated in the experiments in which the catholyte contained 10, 20, and 30% of methanol. These methanol concentrations were used in order to observe substantial differences in the overall rate of dechlorination. The applied potential ( $-0.5 \text{ V}$ ) was the same for these experiments. The results are summarized in Table 1. The recovery values varied slightly between these three experiments. The conversion of 2-CIBP decreased as methanol content increased from 10 to 30%. The rate of 2-CIBP disappearance was higher in solutions with

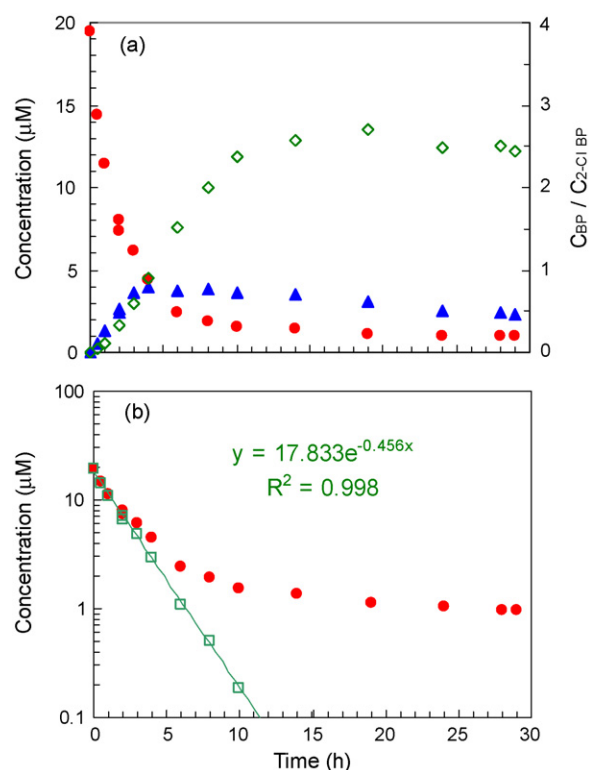


Fig. 2. (a) The profiles of  $C_{2-CIBP}$  (●),  $C_{BP}$  (▲), and the  $C_{BP}/C_{2-CIBP}$  ratio (◇) during dechlorination of 2-CIBP at 0.5 V. (b)  $C_{2-CIBP}$  (●) and  $C_{2-CIBP} - C_{BP}/K'_R$  (□) vs. time in a semi-log plot.  $K'_R$  was obtained by best fitting the data to the exponential line with a maximum  $R^2$  value.  $C_{2-CIBP}$  and  $C_{BP}$  are the concentration of 2-CIBP and BP in the cathode solution;  $K'_R$  is the apparent equilibrium constant.

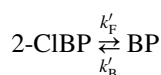


higher methanol content (data not shown in the paper). The (average) values of the biphenyl to 2-CIBP concentration ratios decreased from 5.49 in the solution with 10% methanol to 0.33 in the solution with 30% methanol. The influences on the dechlorination kinetics are discussed in the following section.

## 4. Discussion

### 4.1. Electrochemical equilibrium

The fact that the BP to 2-CIBP concentration ratio reached stabilized values in the second phase suggests that the electrocatalytic dechlorination was a reversible reaction and the reaction obviously approached apparent equilibrium between 2-CIBP and BP:



The rate law for the above overall reaction can be expressed in the following equation:

$$r_{\text{obs}} = k'_F C_{2\text{-CIBP}} - k'_B C_{\text{BP}} \quad (1)$$

where  $C_{2\text{-CIBP}}$  ( $\mu\text{M}$ ) and  $C_{\text{BP}}$  ( $\mu\text{M}$ ) are the concentrations of 2-CIBP and BP in the solution;  $k'_F$  ( $\text{h}^{-1}$ ) and  $k'_B$  ( $\text{h}^{-1}$ ) are the rate constant for the overall forward and backward reactions;  $r_{\text{obs}}$  ( $\mu\text{M h}^{-1}$ ) is the rate of reaction with respect to 2-CIBP concentration in the solution. Based on Eq. (1), the following equations (2)–(5) can be developed for the concentrations and the reaction rate constants:

$$\frac{C_{2\text{-CIBP}} - C_{\text{BP}}/K'_R}{C_{2\text{-CIBP},0} - C_{\text{BP},0}/K'_R} = e^{-k_{\text{adj}} t} = e^{-k'_F(1+(1/K'_R))t} \quad (2)$$

$$K'_R = \frac{k'_F}{k'_B} \quad (3)$$

$$k_{\text{adj}} = k'_F \left( 1 + \frac{1}{K'_R} \right) \quad (4)$$

$$k'_F = \left( \frac{K'_F}{1 + K'_R} \right) k_{\text{adj}} \quad (5)$$

where  $C_{2\text{-CIBP},0}$  ( $\mu\text{M}$ ) and  $C_{\text{BP},0}$  ( $\mu\text{M}$ ) are the initial concentrations of 2-CIBP and BP in the solution;  $K'_R$  is the apparent equilibrium constant for the overall reaction;  $k_{\text{adj}}$  is the adjusted rate constant with respect to  $C_{2\text{-CIBP}} - C_{\text{BP}}/K'_R$ .

Eq. (2) predicts an exponential decline of the  $C_{2\text{-CIBP}} - C_{\text{BP}}/K'_R$  values with time. Such a relationship was demonstrated in Fig. 2(b) for the electrocatalytic dechlorination of 2-CIBP at 0.5 V in 0.1 M  $\text{NH}_4\text{Ac}$ . The value of  $K'_R$  (2.7) used in the figure was obtained by changing its values to maximize the  $R^2$  value in order to best fitting the  $C_{2\text{-CIBP}} - (C_{\text{BP}}/K'_R)$  values to the exponential line. This  $K'_R$  value is very close to the average BP to 2-CIBP concentration ratio ( $2.5 \pm 0.1$ ) obtained in the experiment. The excellent linearity of a plot of  $(C_A - C_B)/K'_R$  versus time in Fig. 2(b) supports the above hypothesis that the electrocatalytic dechlorination is a reversible reaction and the overall reaction approaches equilibrium between 2-CIBP and BP.

Fig. 3(a) plots the values of  $(C_{2\text{-CIBP}} - (C_{\text{BP}}/K'_R))/C_{2\text{-CIBP},0}$  versus time for the dechlorination of 2-CIBP in 0.1 M  $\text{NH}_4\text{Ac}$  at several cathode potentials, and Fig. 3(b) plots the values of  $(C_{2\text{-CIBP}} - (C_{\text{BP}}/K'_R))/C_{2\text{-CIBP},0}$  vs. time for the dechlorination of 2-CIBP at 0.5 V in 0.1 M  $\text{NH}_4\text{Ac}$  solutions with methanol. The values of  $K'_R$  and  $k_{\text{adj}}$ , listed in Table 1, were obtained using the method explained in the previous paragraph, by changing the  $K'_R$  values to get a maximum  $R^2$  value in order to best fit Eq. (1) to the  $(C_{2\text{-CIBP}} - (C_{\text{BP}}/K'_R))/C_{2\text{-CIBP},0}$  values. The values of  $R^2$  and the number of data points used for these fittings also are listed in Table 1. The  $R^2$  values ( $\geq 0.99$ ) resulted from the excellent fitting of  $(C_{2\text{-CIBP}} - (C_{\text{BP}}/K'_R))/C_{2\text{-CIBP},0}$  to the experimental data in a range of two orders of magnitude. Therefore, even though these results were obtained in the experiments that started with relatively high initial concentrations of 2-CIBP and zero concentration of biphenyl (and that the reaction kinetic depends on the (initial) concentrations of 2-CIBP and biphenyl), Eq. (2) should be applicable for the dechlorination of 2-CIBP over a great range

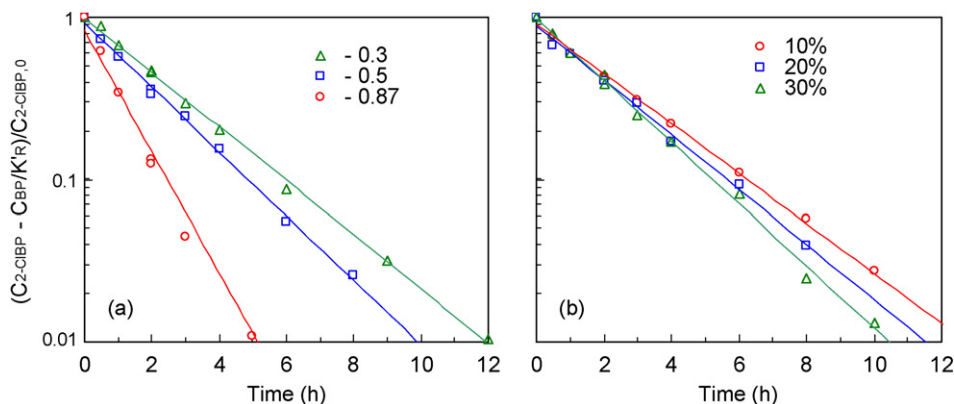
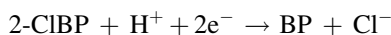


Fig. 3. (a) The profiles of  $(C_{2\text{-CIBP}} - C_{\text{BP}}/K'_R)/C_{2\text{-CIBP},0}$  for the electrolytic dechlorination of 2-CIBP in 0.1 M  $\text{NH}_4\text{Ac}$  solution with a granular-graphite packed electrode at  $-0.3$  V ( $\Delta$ ),  $-0.5$  V ( $\square$ ), and  $-0.87$  V ( $\circ$ ). (b) The profiles of  $(C_{2\text{-CIBP}} - C_{\text{BP}}/K'_R)/C_{2\text{-CIBP},0}$  for the electrolytic dechlorination of 2-CIBP with a granular-graphite packed electrode at  $-0.5$  V in 0.1 M  $\text{NH}_4\text{Ac}$  solutions that contained 10% ( $\circ$ ), 20% ( $\square$ ), and 30% ( $\Delta$ ) methanol.  $C_{2\text{-CIBP}}$  and  $C_{\text{BP}}$  are the concentration of 2-CIBP and BP in the cathode solution;  $K'_R$  is the apparent equilibrium constant.

of concentration. Note that the  $K'_R$  values are slightly different from the concentration ratio. In order to demonstrate our confidence on these  $K'_R$  values, a  $K'_R$  range is provided in Table 1 for each experiment. This range was obtained by changing  $K'_R$  until the residue sum of squares (ssresid) of the fitting is 150% greater than the ssresid value with the listed  $K'_R$  value. These very small ranges indicate little uncertainty of the  $K'_R$  values. The values of  $k'_F$  and  $k'_B$  were calculated from Eqs. (5) and (3), respectively; these values also are listed in Table 1.

The equilibrium constant can be estimated from the free energy change of the half-cell reaction:



The standard free energy change for the above reaction  $\Delta_r G^\circ$  is  $-115.7 \text{ kJ mol}^{-1}$ , based on the standard free energy of formation values 259.6, 0, 275.2, and  $-131.3 \text{ kJ mol}^{-1}$ , respectively, for 2-ClBP,  $\text{H}^+$ , BP, and chloride in the aqueous phase [12,13]. The free energy change value ( $\Delta_r G^{\circ'}$ ) adjusted to the reference state of  $[\text{H}^+] = 10^{-7} \text{ M}$ ,  $[\text{Cl}^-] = 10^{-5} \text{ M}$  is  $-104.3 \text{ kJ mol}^{-1}$  [14], which corresponds to a reduction potential of 0.54 V, and to an equilibrium constant  $K_r = 10^{18.3}$ . The BP to 2-ClBP ratio at equilibrium is  $10^{16.3}$ . The values indicate that the half reaction would proceed thermodynamically to almost completely reduce 2-ClBP to biphenyl.

The applied potential affected significantly the reaction kinetics and equilibrium; the values of  $k_{\text{obs}}$ ,  $k'_F$ , and  $K'_R$  increase as the applied cathode potential increases. The increase of the apparent equilibrium constant  $K'_R$  with the cathode potential indicates that a higher reducing potential favored dechlorination. Such influences of the applied potential on these kinetic and equilibrium parameters are demonstrated clearly in Fig. 4 for the dechlorination of 2-ClBP using the reactor A. The overall forward and backward reaction rate constants had values of  $2\alpha F/RT$  and  $2\beta F/RT$  of  $2.4 \pm 0.8$  and  $3.2 \pm 7.4$ , respectively (here  $\alpha$  and  $\beta$  are the apparent cathodic and anodic transfer coefficient, respectively,  $F$  is the Faraday constant,  $R$  is the gas constant,  $T$  is temperature), which result in values of  $\alpha$  and  $\beta$  of  $0.012 \pm 0.04$  and  $0.015 \pm 0.035$ , respectively. The values of  $2\alpha F/RT$  and  $2\beta F/RT$  for the overall forward and backward reaction rates in reactor B (with different acrylic plastic modules of cathode and anode) in 0.1 M  $\text{NH}_4\text{Ac}$  solutions are  $4.4 \pm 3.4$  and  $6.7 \pm 19.8$ , respectively, and the corresponding values of  $\alpha$  and  $\beta$  are  $0.022 \pm 0.017$  and  $0.034 \pm 0.100$ . The difference between the two  $2\alpha F/RT$  and  $2\beta F/RT$  values for reactors A and B is likely to be due to the difference in making the reactor modules. The very low  $\alpha + \beta$  values suggest that the rate-determining step was not an electron transfer reaction (the  $\alpha + \beta$  value for an electron transfer reaction should be 1). These very low  $\alpha + \beta$  values are consistent with the very low current efficiency data (below 1%) obtained during constant current dechlorination experiments [11]. Low current efficiency, as a result of hydrogen evolution at the cathode, is common for electrolytic dechlorination of chloroaromatics in aqueous solutions [8], and current efficiency

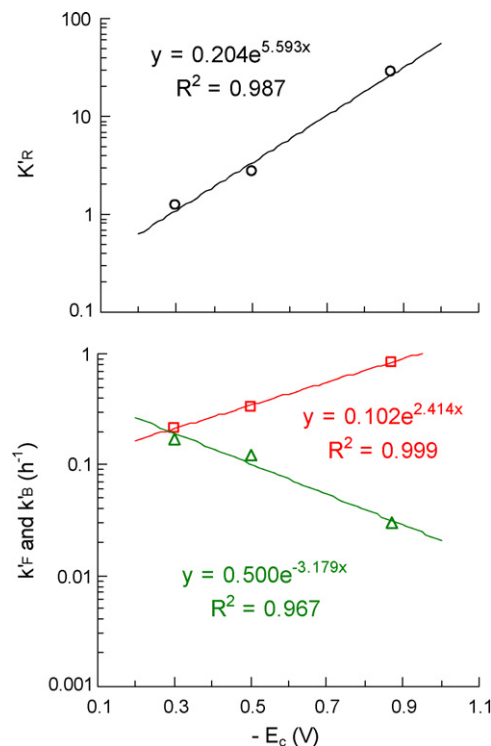


Fig. 4. Dependence of the apparent equilibrium constant  $K'_R$  ( $\circ$ ), the overall forward and backward rate constants  $k'_F$  ( $\square$ ) and  $k'_B$  ( $\triangle$ ) on the cathode potential ( $E_c$ ) for the electrolytic dechlorination of 2-ClBP in 0.1 M  $\text{NH}_4\text{Ac}$  solution at the Pd-loaded granular-graphite packed electrode.

can be improved, to some extent, by part-time application of current or voltage [11].

#### 4.2. Mechanism and rate law

Based on the experimental results that a Pd-free granular graphite electrode did not result in the dechlorination of 2-ClBP [11], and that a pure Pd electrode did not result in the dechlorination of 4-chlorophenol [5], it is likely that the electrocatalytic dechlorination takes place at the Pd–carbon (graphite) interface. Two plausible mechanisms are Langmuir–Hinshelwood (LH) and Rideal–Eley (RE) [15]. The difference between these two mechanisms is that in LH, the reactant is first adsorbed on the surface sites before it reacts, while in RE no such an adsorption step is needed, and the reactant in the liquid phase is involved directly in the surface reaction at either the Pd surface or the Pd–graphite interface. The reaction results in the product, which is then desorbed from the surface sites. The overall reaction rate is determined by one of the steps in these mechanisms. Table 2 lists the expressions for the theoretical overall equilibrium constant  $K_R$  and the overall forward rate constant  $k_F$  and backward rate constant  $k_B$  (based on an overall reaction rate, expressed in Eq. (1)) for all cases when the overall reaction rate is determined by each individual step. For both mechanisms, the expression for  $K_R$  is the same regardless of rate-determining steps. But, these individual steps can be influenced differently by potential and solvent. Applied potential would significantly affect the reaction rate constants ( $k_3$  and  $k_4$  for LH as well as  $k_1$  and  $k_2$  for RE) but not the

Table 2

Parameters for Langmuir–Hinshelwood and Rideal–Eley mechanisms based on rate law  $r_A = k_F C_A - k_B C_B$ 

Mechanisms	Rate-determining step	$k_F$	$k_B$	$1/(1 - \theta)$	$K_R$
Langmuir–Hinshelwood (LH)					
$S + A \rightleftharpoons \frac{1}{2}A_{ad}$	(1)	$k_1(1 - \theta)S_0$	$k_2(k_4/k_3)(k_6/k_5)(1 - \theta)S_0$	$1 + (k_6/k_5)(1 + (k_4/k_3)C_B)$	$(k_1/k_2)(k_3/k_4)(k_5/k_6)$
$A_{ad} + A \rightleftharpoons \frac{3}{4}B_{ad}$	(2)	$k_3(k_1/k_2)(1 - \theta)S_0$	$k_4(k_6/k_5)(1 - \theta)S_0$	$1 + (k_1/k_2)C_A + (k_6/k_5)C_B$	
$B_{ad} \rightleftharpoons \frac{5}{6}B + S$	(3)	$k_5(k_1/k_2)(k_3/k_4)(1 - \theta)S_0$	$k_6(1 - \theta)S_0$	$1 + (k_1/k_2)(1 + (k_3/k_4)C_A)$	
Rideal–Eley (RE)					
$S + A \rightleftharpoons \frac{1}{2}B_{ad}$	(1)	$k_1(1 - \theta)S_0$	$k_2(k_4/k_3)(1 - \theta)S_0$	$1 + (k_4/k_3)C_B$	$(k_1/k_2)(k_3/k_4)$
$B_{ad} + A \rightleftharpoons \frac{3}{4}B + S$	(2)	$k_3(k_1/k_2)(1 - \theta)S_0$	$k_4(1 - \theta)S_0$	$1 + (k_1/k_2)C_A$	

$k_i$  is the rate constant for reaction  $i$ ;  $C_A$  and  $C_B$  are concentrations of A and B in the bulk phase;  $k_F$  and  $k_B$  are the rate constants for the overall forward and backward reactions, respectively;  $K_R$  ( $k_F/k_B$ ) is the equilibrium constant for the overall reaction;  $S_0$  is the total number of sites on the surface;  $\theta$  is the coverage of the surface sites [15].

adsorption and desorption rate constants ( $k_1$ ,  $k_2$ ,  $k_6$ , and  $k_5$  for LH as well as  $k_3$  and  $k_4$  for RE); likewise, solvent would significantly affect the adsorption and desorption steps but not the reaction. The different ways that potential and solvent affected the individual steps, and thus the overall forward and backward rate constants, help differentiate the mechanisms and determine the rate-determining step.

Only mechanisms LH.2 and RE.1 are possible for the dechlorination 2-CIBP because the  $k'_F$  and  $k'_B$  values varied significantly with the applied potential. Mechanism LH.1 is not likely because the  $k_F$  of LH.1, which is the rate constant for the adsorption of 2-CIBP, should not be affected significantly by the cathode potential. The adsorption may be influenced indirectly by the potential, but as the potential increases, the rate of adsorption is likely to decrease because (a) the electrostatic repulsion for PCB molecules with a relatively high negativity increases as the electrode surface gets more negatively charged; and (b) the adsorption at the electrode surface is less favorable due to the generation of more hydrogen gas at the surface. Such a decrease of  $k_F$  with an increasing potential is contrary to the experimental results. Likewise, mechanisms LH.3 and RE.2 are not likely because the  $k_B$  of LH.3 and RE.2, which is the rate constant for BP desorption, should not be affected significantly by the potential. The possibility that the desorption is influenced positively by an increasing potential due to the generation of more hydrogen at the surface is contrary to the experimental results.

However, only mechanism LH.2 is consistent with the experimental results of 2-CIBP dechlorination in methanol solutions. In an LH.2 process, increasing the solvent content will decrease the  $k_F$  value but the  $k_B$  value will be increased, thus leading to a decrease of the  $K_R$  value. In an RE.1 process, adding solvent is likely to increase the  $K_R$  value because the addition of solvent should shift the adsorption equilibrium toward the liquid phase. The results in Table 1 of 2-CIBP dechlorination in methanol solutions indicate that the  $K'_R$  and  $k'_F$  values decrease but the  $k'_B$  values increases as the methanol content increases, which supports the conclusion that the electrocatalytic dechlorination of 2-CIBP likely follows the LH.2 mechanism. This mechanism, which is different from the reaction scheme hypothesized by Tsyganok et al., which involves the formation of the ion–molecule pairs and the adsorption of the associates at the electrode surface [9],

nevertheless is consistent with their experimental results that suggest that the cleavage of the carbon–halogen bond is the rate-determining step for the electrocatalytic dechlorination of chloroaromatic molecules.

#### 4.3. Adsorption and reaction sites

The fact that the electrocatalytic dechlorination of 2-CIBP at a Pd-loaded graphite electrode follows mechanism LH.2 does not indicate at which site(s) of the electrode the dechlorination actually takes place. Mechanism LH.2 certainly is consistent with the reaction scheme proposed by Cheng et al. [5] that 2-CIBP is adsorbed at the graphite surface along the Pd–graphite interface and is dechlorinated by the highly reactive hydrides (which are generated whenever the electrode is polarized) on the Pd surface. However, the proposed scheme was based on the results of dechlorination of 4-chlorophenol (not a PCB congener) at a Pd electrode, a carbon felt electrode, and a Pd-loaded carbon felt electrode.

We reasonably can conclude that an electrode of Pd (or Pd surface) could not cause the direct electrochemical reduction of 2-CIBP under similar conditions, based on our previous experimental result that a granular graphite-packed electrode did not cause dechlorination of 2-CIBP [11] and experimental results in the literature. PCBs were reductively dechlorinated electrochemically at a mercury and lead cathode [2,3], but at potentials higher than the standard reduction potentials (2.369 V vs. SCE for 2-CIBP) in a bicontinuous microemulsion of surfactant/oil/water with catalysts of zinc phthalocyanine or nickel phthalocyanine. With a standard reduction potential higher than that of 4-chlorophenol, which was not directly reduced at a Pd electrode, 2-CIBP will not be reduced electrochemically at the Pd electrode.

It has been hypothesized that PCBs were electrocatalytically dechlorinated through hydrogenolysis at the Pd–carbon interface or at the Pd surface in a water–methanol medium with tetra-alkylammonium ( $R_4N^+$ ) salts [6,9]. According to Tsyganok et al., the  $R_4N^+$  ions form ion–molecule pairs with the haloaromatic molecules: the ion–molecule associate adsorbs on the Pd surface or on the Pd–carbon interface area, and the carbon–halogen bond of the chloroaromatics molecule is attacked by the highly reactive hydrides generated on the Pd surface. The dechlorination of the chloroaromatic molecules at

the Pd surface is facilitated by the  $R_4N^+$  ion through the ion–molecule association. This hypothesis was developed based on the effects of the  $R_4N^+$  molecular size on the reaction extent, the current efficiency and the total organic recovery. However, these effects also can be explained by the coverage of the  $R_4N^+$  ions on both the Pd–carbon interface and the Pd surface during the dechlorination at the Pd–carbon interface. The facilitation of  $R_4N^+$  ions for the adsorption and dechlorination of haloaromatic molecules at a Pd surface needs to be supported by the results of dechlorination at a Pd electrode (not a Pd-loaded carbon felt electrode).

These published results are consistent with the results obtained in our experiments: (a) there were no  $R_4N$  salts to facilitate adsorption of 2-CIBP at a Pd surface; (b) the cathode potential was much lower than the standard reduction potential of 2-CIBP; (c) the dechlorination reaction was the rate-determining step; (d) the rate-determining step was not an electron transfer reaction. Therefore, at a Pd-loaded granular-graphite electrode, 2-CIBP was adsorbed at the carbon surface (not the Pd surface) along the carbon–Pd interface and was dechlorinated by the reactive hydrides generated at the Pd surface. The potential dependence of the overall forward reaction rate constants  $k'_F$  and  $k_F$  was a result of the potential dependence of the reaction rate constant  $k_3$ . The reaction rate constant  $k_3$  was related to the hydride concentration at the Pd surface, which is a function of the applied potential ( $E_c$ ) [16]. Based on this information, the dechlorination process is expected to be improved by increasing the system pressure to increase the surface concentration of hydrogen atoms and by increasing Pd–carbon interface with a high concentration of Pd colonies of smaller diameters at a porous graphite surface.

## 5. Conclusions

Consistent with the results of our previous study using a Pd-loaded granular graphite-packed electrode, the dechlorination of 2-CIBP, both at different potentials and in methanol–water solutions, did not follow the first order kinetics. The electrocatalytic dechlorination had obviously reached apparent equilibrium in the experiments. The apparent equilibrium constant, as well as the overall forward and backward rate constants, varied with the potential. The potential dependence follows the Tafel equation, but with very small apparent electron transport coefficient values. The potential dependence suggests a reaction mechanism in which the electrocatalytic reaction is the rate-determining step. Inferred from the influence of methanol on the overall rate and equilibrium constants, the electrocatalytic process likely followed the Langmuir–Hinshelwood mechanism. It is believed that 2-CIBP first was adsorbed at the carbon surface (not the Pd surface) along the carbon–Pd interface and was dechlorinated by the

reactive hydrides generated at the Pd surface. The potential dependence of the dechlorination rate was an effect of the potential on the concentration of the hydrides at the Pd surface.

To establish this technology as a viable remediation tool, studies are needed to evaluate the gradual loss of catalyst activity over an extensive period of time and to develop an effective method to reactivate the Pd-loaded granular graphite electrode. Furthermore, a complete determination of the mechanism and the values of the rate constants for each individual step requires rigorous modeling of results from extensive experiments of dechlorination and adsorption under various conditions. Also the extension of this research to the dechlorination of other PCB congeners should consider a series of consecutive steps of chlorine elimination during the electrocatalytic process.

## Acknowledgements

This work was performed at and financially supported by the National Risk Management Research Laboratory of the U.S. Environmental Protection Agency. This paper has not been subjected to the Agency's internal review. Therefore, the research results presented herein do not, necessarily, reflect the views of the Agency or its policy.

## References

- [1] S.O. Farwell, F.A. Beland, R.D. Geer, *Electroanal. Chem. Interf. Electrochem.* 61 (1975) 315–324.
- [2] J.F. Rusling, C.N. Shi, S.L. Suib, *J. Electroanal. Chem.* 245 (1988) 331–337.
- [3] S. Zhang, J.F. Rusling, *Environ. Sci. Technol.* 27 (1993) 1375–1380.
- [4] S.M. Kulikov, V.P. Plekhanov, A.I. Tsyganok, C. Schlimm, E. Heitz, *Electrochim. Acta* 41 (1996) 527–531.
- [5] I.F. Cheng, Q. Fernando, N. Korte, *Environ. Sci. Technol.* 31 (1997) 1074–1078.
- [6] A.I. Tsyganok, K. Otsuka, I. Yamanaka, *J. Electrochem. Soc.* 145 (1998) 3844–3850.
- [7] C.-H. Lin, S.-K. Tseng, *Chemosphere* 39 (1999) 2375–2389.
- [8] E. Szebenyi-Gyori, E. Gagy-Palfy, G. Bajnoczy, E. Prepostffy, *Period. Polytech. Ser. Chem. Eng.* 43 (1999) 65–76.
- [9] A.I. Tsyganok, I. Yamanaka, K. Otsuka, *Chemosphere* 39 (1999) 1819–1831.
- [10] P. Dabo, A. Cyr, F. Laplante, F. Jean, H. Menard, J. Lessard, *Environ. Sci. Technol.* 34 (2000) 1265–1268.
- [11] Y. Fang, S.R. Al-Abed, *Chemosphere* 66 (2007) 226–233.
- [12] D.A. Holmes, B.K. Harrison, *Environ. Sci. Technol.* 27 (1993) 725–731.
- [13] R.P. Schwarzenbach, P.M. Gschwend, D.M. Imboden, *Environmental Organic Chemistry*, 2nd ed., Wiley-Interscience, 2003.
- [14] T.M. Vogel, C.G. Criddle, P.L. McCarty, *Environ. Sci. Technol.* 21 (1987) 722–736.
- [15] R.I. Masel, *Principles of Adsorption and Reaction on Solid Surfaces*, John Wiley & Sons Inc., 1996.
- [16] P.H. Rieger, *Electrochemistry*, 2nd ed., Chapman & Hall Inc., 1994.